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(54) Process for the preparation of complex perovskite type compounds.

(57) The present invention provides a process for producing powder of complex perovskite type compounds by using metal alkoxides. In the prior art, methods were known for synthesizing crystalline powder of simple perovskite type compounds such as  $\text{BaTiO}_3$ . According to the conventional methods, however, when synthesizing a complex perovskite type compound having two atoms of different valences at the B site of perovskite structure by hydrolyzing metal alkoxides, there could be obtained only amorphous powder, and for crystallizing it, heating to a temperature of around 600 to 800°C was necessary.

According to the process of this invention, it is possible to synthesize the crystalline complex perovskite type compounds at a low temperature of around 100°C, which is 500 to 700°C lower than the temperature required in the conventional methods, by adjusting the amount of water added according to the type of the solvent used and controlling the reaction temperature at a specified level or higher.

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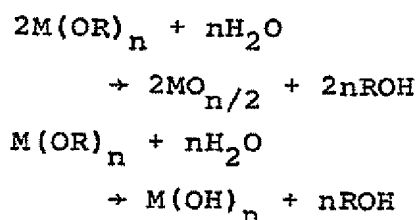
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PROCESS FOR THE PREPARATION OF  
COMPLEX PEROVSKITE TYPE COMPOUNDS

0237087

1 BACKGROUND OF THE INVENTION

Attention has been focused recently on the hydrolysis of metal alkoxides as new techniques for producing base powder for ceramics. This method makes use of the peculiar property of the metal alkoxides of the formula  $M(OR)_n$  (wherein M is a metal atom of  $n$  valences and R is an alkyl group) that they are reacted with water to produce metal oxides or hydroxides and an alcohol according to the following reaction formula:



10 The powder of  $TiO_2$  or  $SiO_2$  synthesized by this method is particulate, narrow in particle size distribution and also high in purity, so that it has high availability as a powder material for ceramics.

It has been also practiced in the art to  
15 synthesize the oxides containing two or more type of metals by the hydrolysis of a mixed solution of two or more types of metal alkoxides. For example,  $BaTiO_3$  having a perovskite structure is synthesized by dissolving barium alkoxide and titanium alkoxide in a

1 1:1 molar ratio in an organic solvent and adding water  
dropwise to the mixed solution to effectuate the hydro-  
lysis thereof (see Japanese Patent Kokai (Laid-Open)  
No. 82119/82). According to the conventional method in  
5 which  $\text{BaCO}_3$  and  $\text{TiO}_2$  are mixed and calcined, a high  
temperature of around  $1,000^\circ\text{C}$  is required for the  
synthesis of  $\text{BaTiO}_3$ , but when said metal alkoxides  
hydrolysis method is employed, it is unnecessitated to  
use such a high temperature and crystalline  $\text{BaTiO}_3$  can  
10 be obtained by controlling the temperature of the  
solution at  $60$  to  $70^\circ\text{C}$ . Therefore, the products by this  
hydrolysis method had many advantages over those by the  
conventional method, such as no fear of contamination  
by the impurities at the time of mixing of the materials  
15 by a ball mill or such and no possibility of suffering  
from an increase of particle size or a drop of surface  
activity which could be caused by a high-temperature heat  
treatment.

As the oxides containing two or more types of  
20 metals and synthesizable as a crystalline powder by said  
hydrolysis method, there are known the perovskite type  
compounds such as  $\text{SrTiO}_3$ ,  $\text{Ba}(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$ ,  $\text{BaZrO}_3$  and  
 $(\text{Ba}_{1-x}\text{Sr}_x)\text{TiO}_3$  and their solid solutions (Japanese  
Patent Kokai No. 2220/83); ferrite compounds such as  
25  $\text{MnFe}_2\text{O}_4$ ,  $(\text{Mn}_{1-x}\text{Zn}_x)\text{Fe}_2\text{O}_4$  and  $\text{NiFe}_2\text{O}_4$  (Japanese Patent  
Kokai No. 26726/82); germanates such as  $\text{SrGeO}_3$ ,  $\text{PbGeO}_3$   
and  $\text{ZnGeO}_4$  (Japanese Patent Kokai No. 19971/83);  $\text{PbWO}_4$ ,  
 $\text{SrAs}_2\text{O}_6$ , etc.

1                    However, when it is tried to synthesize **Q237081**  
complex perovskite type compound having a more complicate  
structure and represented by the general formula  
 $A(B_x, C_y)O_3$  (where A, B and C are the metal atoms of  $p$ ,  
5  $q$  and  $r$  valences, respectively, and  $q \neq r$ ,  $x + y = 1$ , and  
 $xq + yr = 6 - p$ ) by using said hydrolysis method, there  
can be synthesized only the amorphous-state powders  
when the ordinarily used techniques are employed, and for  
crystallizing them, heating to a temperature of around  
10 500 to 700°C is required. Thus, in the synthesis of such  
compounds by the hydrolysis method using the conventional  
techniques, efficient use was not made of the merit of  
this hydrolysis method in being capable of low-temperature  
synthesis of ultrafine particles.

#### 15 SUMMARY OF THE INVENTION

The present invention provides a process for  
producing the complex perovskite type compound represented  
by the chemical formula:  $A(B_x, C_y)O_3$  (wherein A, B and  
C are the metal atoms of  $p$ ,  $q$  and  $r$  valences, respec-  
20 tively, and  $q \neq r$ ,  $x + y = 1$ , and  $xq + yr = 6 - p$ ),  
characterized in that three types of metal alkoxids:  
 $A(OR_1)_p$ ,  $B(OR_2)_q$  and  $C(OR_3)_r$  (wherein  $R_1$ ,  $R_2$  and  $R_3$  are  
each an alkyl group), weighed to  $a$ ,  $b$  and  $c$  moles,  
respectively, are mixed with an organic solvent contain-  
25 ing  $z\%$  by volume of a non-polar organic solvent and  
(100 -  $z$ )% by volume of a polar organic solvent, then  
water or a mixed solution of water and an organic solvent

1 is added thereto so that the amount of water will become  
(8 - 0.065z) x (ap + bq + cr) moles or greater to hydro-  
lyze the metal alkoxides, the reaction mixture being  
heated to 85°C or above in the presence of water/organic  
5 solvent, at least in the course of or after the hydrolysis  
reaction, and then the solvent is removed.

As a result of the longtime studies, the  
present inventors found that in the synthesis of complex  
perovskite type compounds by the hydrolytic reaction of  
10 metal alkoxides, it is possible to synthesize a  
crystalline powder of complex perovskite type compound,  
which has been considered impossible with the prior art,  
by specifying, among the synthesizing conditions, the  
type of the organic solvent used, the amount of water  
15 added and the solution heating temperature as defined  
above. The present invention disclosed herein is based  
on this finding. The present inventors consider that said  
hydrolytic reaction is allowed to proceed in the desired  
way to produce an amorphous-state precursor by the proper  
20 selection of said two reaction conditions, viz. the  
type of the organic solvent used and the amount of water  
added, and the occurrence of crystallization of said  
amorphous compound owes to the proper selection of the  
temperature at which the reaction solution is heated.

25 According to the studies by the present  
inventors, in order to synthesize a complex perovskite  
type compound from metal alkoxides, it is essential that  
the two conditions - that the hydrolytic reaction proceeds

1 at a sufficiently high rate, and that the crystallization  
is induced by heating to a temperature of or above a  
certain level, at least in the course of or after the  
hydrolysis reaction - be met at the same time. It is  
5 possible to let the hydrolytic reaction proceed at a  
sufficiently high rate by adding water in large excess or  
by using a non-polar solvent. The amount of water  
necessary for forming a crystalline precipitate is  
decided depending on the amount of the non-polar solvent  
10 in the solvent used for the reaction. If the amount of  
water added is too large, in case the reaction material  
contains alkali or alkali earth metals whose hydroxides  
have high water solubility, their metal ions may be  
eluted out to cause a change of composition. In actual  
15 practice, therefore, it is desirable to use a system with  
as high a content of non-polar solvent as possible  
(preferably 90 to 100% by volume of non-polar solvent in  
the whole solvent used) and carry out the hydrolysis with  
a small amount of water.

20 The reason why the hydrolytic reaction is  
accelerated by the use of a non-polar solvent may pro-  
bably be as follows: the non-polar solvents, although  
soluble in alcohols, have almost no compatibility with  
water, so that when water is added to the system, there  
25 are partly created in the system the areas where the  
concentration of water is extremely high, and the  
hydrolysis advances rapidly in such areas. The promotion  
of hydrolysis by the increase of the amount of water

1 added is also considered attributable to the increase of  
water concentration in the system.

However, even if the hydrolysis is allowed to  
proceed in this way, the formed precipitate will still  
5 remain amorphous in the state of precursor if the  
temperature is below 80°C, and if it is dried as it is  
at low temperature, there can be obtained no crystalline  
precipitate, and even if the precipitate is heated after  
drying, it hardly becomes crystalline. For achieving  
10 crystallization, it is necessary to heat the system to a  
temperature of or above 85°C, at least in the course of  
or after the hydrolytic reaction.

The term "non-polar solvent" used here refers  
to the organic solvents with extremely low compatibility  
15 with water, such as benzene, toluene, xylene, cumene,  
ethylbenzene, n-hexane, n-hexyl alcohol and the like, and  
the term "polar solvent" refers to those organic solvents  
which have high compatibility with water, such as  
methanol, ethanol, n-propanol, isopropanol, n-butanol,  
20 acetone and the like.

The present invention will hereinafter be  
described by showing the examples thereof, but it will be  
obvious that these examples are merely intended to be  
illustrative and not limitive of the embodiments of  
25 the invention.

#### Example 1

Barium isopropoxide, tantalum isopropoxide and

1 zinc isopropoxide were weighed to be 0.012 moles, 0.004  
moles and 0.008 moles, respectively, so that the Ba:Zn:Ta  
ratio would become 3:1:2. These materials were mixed in  
120 ml of a xylene/isopropyl alcohol mixed solvent and  
5 the mixture was put into a flask. The flask was set in  
an oil bath and the mixture therein was refluxed under  
heating at 75°C in an N<sub>2</sub> stream for 2 hours. Then a  
water/isopropyl alcohol (1:1) mixed solvent was added to  
the mixture under stirring while changing the amount of  
10 water manifoldly, after which the temperature of the oil  
bath was raised to 120°C and refluxing of the mixture was  
continued at this temperature. The resultantly formed  
precipitate was separated by a centrifuge and, while in  
a wet state, wrapped up in filter paper. It was further  
15 enshrouded twofold in parchment paper to retard escape of  
vapor and then dried in a dryer set at 120°C to form  
powder. As a result of these operations, the vapor pres-  
sure became higher than 1 atm., and even in the reaction  
system with a boiling point below 85°C, the temperature  
20 of the sample became higher than 85°C before it was  
perfectly dried. The perfectly dried powders were  
subjected to X-ray diffractometry, the results of which  
are shown in Table 1.



Table 1: X-ray diffraction of the products **0237081**

		Ratio of propyl alcohol, vol%						
		0	5	10	30	50	75	100
Amount of water added (mol)	0.072	Am	Am	Am	Am	Am	Am	Am
	0.108	P.Cr	Am	Am	Am	Am	Am	Am
	0.144	Cr	P.Cr	Am	Am	Am	Am	Am
	0.216	G.Cr	Cr	P.Cr	Am	Am	Am	Am
	0.288	G.Cr	Cr	Cr	P.Cr	Am	Am	Am
	0.428	G.Cr	G.Cr	Cr	P.Cr	P.Cr	Am	Am
	0.567	P.Cr	Cr	Cr	Cr	P.Cr	P.Cr	P.Cr
	0.720	P.Cr	P.Cr	P.Cr	P.Cr	Cr	P.Cr	P.Cr
	0.864	P.Cr	P.Cr	P.Cr	P.Cr	P.Cr	Cr	Cr
	3.6	P.Cr	P.Cr	P.Cr	P.Cr	P.Cr	P.Cr	P.Cr

Am: amorphous; Cr: crystallinity to medium degree;

P.Cr: low crystallinity; G.Cr: high crystallinity

1 As seen from Table 1, in case xylene, a non-  
polar organic solvent, alone was used as solvent, the  
crystal phase of  $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$  began to form with  
additional of only 0.108 moles of water, or merely 1.5  
5 or so times the amount of water necessary for barium  
isopropoxide, zinc isopropoxide and tantalum isopropoxide  
to react with all amount of water added and hydrolyze  
wholly into hydroxides. However, when the amount of  
xylene was decreased while proportionally increasing  
10 isopropyl alcohol which is a polar organic solvent, the

1 amount of water required for forming the crystal phase  
increased accordingly, and when the ratio of isopropyl  
alcohol became 100%, addition of water in an amount of  
0.576 moles, or more than 8 times the amount of water  
5 necessary for the hydrolysis of said metal alkoxides,  
was required for forming the crystal phase. Whichever  
the type of solvent used is, the crystallinity of the  
formed precipitate lowers when the amount of water added  
become excessive. This is probably because  $\text{Ba}(\text{OH})_2$ , the  
10 hydrolyzate of barium isopropoxide, is dissolved in  
excess water.

#### Example 2

Barium isopropoxide, tantalum ethoxide and  
zinc n-propoxide were weighed to be 0.006 moles, 0.002  
15 moles and 0.004 moles, respectively, so that the Be:Zn:Ta  
ratio would become 3:1:2. These materials were mixed  
in 120 ml of xylene and refluxed under heating at 65°C  
in an  $\text{N}_2$  stream for 2 hours. Then 0.108 moles of water  
was added thereto under stirring, and the mixture was  
20 further refluxed under heating at 65°C for one hour.  
A part of the produced precipitate was sampled out and  
subjected to X-ray diffraction in a wet state. It was  
amorphous. So, the reaction temperature was further  
raised, and reflux was carried out at 80°C, 85°C, 90°C  
25 and 105°C for 2 hours and the synthesized samples were  
centrifuged to separate the solvent and then subjected  
to X-ray diffraction in a wet state. As a result, the

1 sample obtained after reaction at 80°C still had the  
amorphous phase. In the case of the sample obtained  
after 85°C reaction, its diffraction pattern showed  
a peak, though very broad, due to the crystal phase of  
5  $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$ . Crystal phase was produced in the  
samples dried at 90°C and above. The particle size of  
the sample dried at 105°C was measured by the BET method  
and X-ray diffractometry. It was approximately 0.04  
microns.

### 10 Example 3

Barium isopropoxide, zinc isopropoxide and  
niobium isopropoxide were weighed to be 0.012 moles,  
0.004 moles and 0.008 moles, respectively, so that the  
Ba:Zn:Nb molar ratio would become 3:1:2. These materials  
15 were mixed in 120 ml of mixed solutions of xylene and  
isopropyl alcohol of various mixing ratios, and each  
mixture was put into a flask. The flask was set in an  
oil bath and the mixture therein was refluxed under  
heating at 75°C in an  $\text{N}_2$  stream for 2 hours. Then a  
20 1:1 mixed solution of water and isopropanol was added  
thereto under stirring by changing the amount of water  
manifoldly, after which the oil bath temperature was  
raised to 120°C and reflux was continued under this  
condition. The resultantly formed precipitate was  
25 separated by a centrifuge, then wrapped up in a wet state  
in filter paper, further wrapped twofold in parchment  
paper to make vapor hard to escape and dried in a dryer

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1 set at 120°C to form powder. As a result of these operations, the vapor pressure became higher than 1 atm., and even in the reaction system with a boiling point below 85°C, the temperature of the sample became higher than 85°C before it was perfectly dried. Examinations of the perfectly dried powders by X-ray diffraction gave the results shown in Table 2.

Table 2: X-ray diffraction of the products

		Ratio of propyl alcohol, vo. %						
		0	5	10	30	50	75	100
Amount of water added (moles)	0.072	Am	Am	Am	Am	Am	Am	Am
	0.108	P.Cr	Am	Am	Am	Am	Am	Am
	0.144	P.Cr	P.Cr	Am	Am	Am	Am	Am
	0.216	Cr	P.Cr	P.Cr	Am	Am	Am	Am
	0.288	Cr	Cr	P.Cr	P.Cr	Am	Am	Am
	0.428	Cr	Cr	P.Cr	P.Cr	P.Cr	Am	Am
	0.576	P.Cr	Cr	P.Cr	P.Cr	P.Cr	P.Cr	P.Cr
	0.720	P.Cr	P.Cr	P.Cr	P.Cr	P.Cr	P.Cr	P.Cr
	0.864	P.Cr	P.Cr	P.Cr	P.Cr	P.Cr	P.Cr	P.Cr
	3.6	P.Cr	P.Cr	P.Cr	P.Cr	P.Cr	P.Cr	P.Cr

Am: amorphous; Cr: crystalline; P.Cr: low crystallinity.

As seen from Table 2, in case xylene, a non-polar organic solvent, alone was used as solvent, the crystal phase of  $\text{Ba}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$  began to form with

1 addition of only 0.108 moles of water, or 1.5 or more  
times the amount of water necessary for barium isopropoxide, zinc isopropoxide and niobium isopropoxide  
to react with all amount of water added and hydrolyze  
5 wholly into hydroxides. However, when the amount of  
xylene was decreased while proportionally increasing  
the amount of isopropyl alcohol which is a polar  
organic solvent, the amount of water required for forming  
the crystal phase increased accordingly, and when the  
10 ratio of isopropyl alcohol became 100%, addition of  
water in an amount of 0.576 moles, or more than 8 times  
the amount necessary for the hydrolysis of said metal  
alkoxides, was required for forming the crystal phase.  
Whichever the type of solvent used is, the crystallinity  
15 of the produced precipitate lowers when an excess amount  
of water is added. This is probably because  $\text{Ba}(\text{OH})_2$ ,  
the hydrolyzate of barium isopropoxide, is dissolved in  
excess water.

#### Example 4

20 Barium isopropoxide, zinc n-propoxide and  
niobium ethoxide were weighed to be 0.006 moles, 0.002  
moles and 0.004 moles, respectively, so that the Ba:Zn:Nb  
molar ratio would become 3:1:2. These materials were  
mixed in 120 ml of n-hexanol and refluxed under heating  
25 at 65°C in an  $\text{N}_2$  stream for 2 hours. Then 0.108 moles  
of water was added thereto under stirring, and the  
mixture was further refluxed under heating at 65°C for

1 one hour. A part of the resulting precipitate was  
sampled out and subjected in a wet state to X-ray  
diffraction, which showed the precipitate was amorphous.  
So, the reaction temperature was further raised, and the  
5 mixture was refluxed at 80°C, 85°C, 90°C and 105°C for  
2 hours and the obtained samples were centrifuged to  
separate the solvent and subjected in a wet state to  
X-ray diffraction. The results showed that the sample  
which had undergone 80°C reaction was amorphous, while  
10 the diffraction pattern of the sample dried at 85°C  
exhibited a peak, though very broad, of crystal phase  
of  $\text{Ba}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ . Crystal phase was seen produced  
in the samples dried at 90°C and 105°C.

#### Example 5

15 Strontium isopropoxide, magnesium isopropoxide  
and niobium isopropoxide were weighed to be 0.012 moles,  
0.004 moles and 0.006 moles, respectively, so that the  
Sr:Mg:Nb molar ratio would become 3:1:2. These materials  
were mixed in 120 ml of mixed solutions of xylene and  
20 isopropyl alcohol of various ratios, and each mixture  
was put into a flask. The flask was set in an oil bath  
and the mixture therein was refluxed under heating at  
75°C in an  $\text{N}_2$  stream for 2 hours. Then a 1:1 mixed  
solution of water and isopropyl alcohol was added thereto  
25 under stirring while changing the amount of water  
manifoldly, after which the oil bath temperature was  
raised to 120°C and the mixture was further refluxed at

1 this temperature. Each of the resultantly formed pre-  
 precipitate was separated by a centrifuge, wrapped up in a  
 wet state in filter paper, further wrapped twofold in  
 parchment paper to deter escape of vapor and then dried  
 5 at 120°C to obtain powder. Owing to these operations,  
 the vapor pressure became higher than 1 atm., and even in  
 the reaction system with a boiling point below 85°C, the  
 sample temperature became higher than 85°C before it was  
 perfectly dried. The perfectly dried powders were  
 10 examined by X-ray diffraction to obtain the results  
 shown in Table 3.

Table 3: X-ray diffraction of the products

		Ratio of propyl alcohol, vol%						
		0	5	10	30	50	75	100
Amount of water added (moles)	0.072	Am	Am	Am	Am	Am	Am	Am
	0.108	P.Cr	Am	Am	Am	Am	Am	Am
	0.144	Cr	Cr	Am	Am	Am	Am	Am
	0.216	Cr	Cr	P.Cr	Am	Am	Am	Am
	0.288	P.Cr	P.Cr	P.Cr	P.Cr	Am	Am	Am
	0.428	P.Cr	P.Cr	P.Cr	P.Cr	P.Cr	Am	Am
	0.576	P.Cr	P.Cr	P.Cr	P.Cr	P.Cr	P.Cr	P.Cr
	0.720	P.Cr	P.Cr	P.Cr	P.Cr	P.Cr	P.Cr	P.Cr
	0.864	P.Cr	P.Cr	P.Cr	P.Cr	P.Cr	P.Cr	P.Cr
	3.6	P.Cr	P.Cr	P.Cr	P.Cr	P.Cr	P.Cr	P.Cr

Am: amorphous; Cr: crystalline; P.Cr: low crystallinity.

1 As seen from Table 3, in case xylene (a non-  
polar organic solvent) alone was used as solvent, the  
crystal phase of  $\text{Sr}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  began to form with  
addition of only 0.108 moles of water, or 1.5 or more  
5 times the amount of water necessary for strontium iso-  
propoxide, magnesium isopropoxide and niobium isopro-  
poxide to react with all amount of water added and  
hydrolyze wholly into hydroxides. However, when the  
amount of xylene was decreased while proportionally  
10 increasing the ratio of isopropyl alcohol which is a  
polar organic solvent, the amount of water required for  
forming the crystal phase increased accordingly, and  
when the ratio of isopropyl alcohol became 100%, addition  
of water in an amount of 0.576 moles, or more than 8  
15 times the amount necessary for the hydrolysis of said  
metal alkoxides, was required for forming the crystal  
phase. Whichever the type of solvent used was, the  
crystallinity of the produced precipitate lowered when  
the amount of water added was too large. This is probably  
20 because  $\text{Sr}(\text{OH})_2$ , the hydrolyzate of strontium isopro-  
poxide, was dissolved in excess water.

#### Example 6

Strontium isopropoxide, magnesium n-propoxide  
and niobium ethoxide were weighed to be 0.006 moles, 0.002  
25 moles and 0.004 moles, respectively, so that the Sr:Mg:Nb  
molar ratio would become 3:1:2. These materials were  
mixed in 120 ml of xylene and refluxed under heating at



1 65°C in an N<sub>2</sub> stream for 2 hours. Then a 1:4 mixed  
solution of water and ethanol was added to the refluxed  
mixture under stirring so that the amount of water  
become 0.072 moles, and the mixture was further refluxed  
5 under heating at 65°C for one hour. The resultantly  
formed precipitate was sampled out and subjected in a  
wet state to X-ray diffraction, which showed the pre-  
cipitate was amorphous. So, the reaction temperature  
was further raised, and reflux was carried out at 80°C,  
10 85°C, 90°C and 105°C and the synthesized samples were  
filtered to separate the substantial part of the solvent  
and then subjected in a wet state to X-ray diffractometry.  
It was found that the sample dried at 80°C was amorphous  
while the sample dried at 85°C showed a diffraction peak,  
15 though very broad, of the crystal phase of  $\text{Sr}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{-O}_3$ .  
Formation of crystal phase was evident in the samples  
dried at 90°C and above.

Here, the reaction conditions are briefly  
described. The higher the metal alkoxide/organic  
20 solvent mixing ratio, the better becomes the crystal-  
linity of the produced precipitate, but a too high  
mixing ratio leads to difficult handling of the product  
as the produced precipitate/organic solvent ratio  
increases. As regards water added, the higher the rate  
25 of addition of water, the better becomes the crystal-  
linity of the produced precipitate. In case of diluting  
water added with a polar organic solvent, it is of  
course necessary to be attentive to the change of water

1 addition rate, but the effect derived from the incorpora-  
tion of an organic solvent in the system for the purpose  
of dilution is smaller than the effect due to the casual  
presence of such solvent in the system before the hydro-  
5 lysis, so that the effect by the incorporation of said  
solvent, if small in amount, may be disregarded. The  
synthesis can be also achieved by using other methods,  
such as adding water in the form of vapor or adding a  
metal alkoxide/organic solvent mixed solution dropwise  
10 to water.

Even with a system with a high content of  
polar organic solvent, it is possible to produce a  
crystalline precipitate by increasing the amount of  
water added, but if the amount of water added is too  
15 large, in case alkali earth metals or such are contained  
as metal component, the hydroxides thereof may be dis-  
solved in water because of their high solubility in  
water, causing a decrease of crystallinity or a composi-  
tional deviation. For avoiding this, it is a possible  
20 measure to add beforehand such metal alkoxides in a  
somewhat greater amount than the essential compositional  
requirement, but since such measure makes it more  
difficult to control the reaction, it is desirable to  
use a system with as high a content of non-polar organic  
25 solvent as possible and carry out the hydrolysis with  
a small amount of water.

1. A process for preparing a complex perovskite type compound, which comprises weighing out three types of metal alkoxides represented by the formulae  $A(OR_1)_p$ ,  $B(OR_2)_q$  and  $C(OR_3)_r$  (wherein A, B and C are metal atoms of p, q and r valences, respectively,  $q \neq r$ , and  $R_1$ ,  $R_2$  and  $R_3$  are each an alkyl group) so that their amounts will become a moles, b moles and c moles, respectively, mixing them with an organic solvent containing z% by volume of a non-polar organic solvent and (100 - z)% by volume of a polar organic solvent (wherein  $0 \leq z \leq 100$ ), adding thereto water or a mixed solution of water and an organic solvent so that the amount of water will become  $(8 - 0.065z) \times (ap + bq + cr)$  moles or greater to hydrolyze the metal alkoxides, heating the hydrolyzate in the presence of water/organic solvent at a temperature of 85°C or higher, at least in the course of or after the hydrolysis reaction, and then removing the solvent to obtain a crystalline compound represented by the chemical formula  $A(B_x, C_y)O_3$  (wherein  $X + y = 1$ , and  $xq + yr = 6 - p$ ).
2. The process according to claim 1, wherein A is an alkali earth metal, and B and C are each an element selected from Mg, Zn, Nb, Ta, Co and Ni.
3. The process according to claim 1 or 2, wherein the non-polar organic solvent used is benzene, toluene, xylene, cumene, ethylbenzene, hexane, pentanol, hexanol or heptanol.

anyone of

4. The process according to/claims 1/<sup>to 3</sup> wherein the polar organic solvent used is methanol, ethanol, propanol or butanol.

anyone of / to 4

5. The process according to/claims 1/ wherein the organic solvent used is one having a boiling point of 85°C or higher, and the heating after addition of water is carried out at the boiling point or below of said organic solvent under 1 atmosphere.

anyone of / to 5

6. The process according to/claims 1/ wherein the organic solvent used is one having a boiling point below 85°C, and the heating after addition of water is carried out under a pressure of 1 atm. or higher to make the temperature of the system 85°C or higher.

anyone of / to 6

7. The process according to/claims 1/ wherein when water is added, the water added is diluted 1 time or more with a polar organic solvent.

anyone of / to 7

8. The process according to/claims 1/ wherein the course of heating before and after addition of water, evaporation of the solvent is prevented by using a reflux condenser.

anyone of / to 8

9. The process according to/claims 1/ wherein the separation of the precipitate and the solvent is accomplished by filtration or centrifuging.

anyone of / to 9

10. The process according to/claims 1/ wherein the heating at the time of reaction is effected by a water bath, oil bath or electric heater.

(19)



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(54) **Process for the preparation of complex perovskite type compounds.**

(57) The present invention provides a process for producing powder of complex perovskite type compounds by using metal alkoxides. In the prior art, methods were known for synthesizing crystalline powder of simple perovskite type compounds such as BaTiO<sub>3</sub>. According to the conventional methods, however, when synthesizing a complex perovskite type compound having two atoms of different valences at the B site of perovskite structure by hydrolyzing metal alkoxides, there could be obtained only amorphous powder, and for crystallizing it, heating to a temperature of around 600 to 800°C was necessary.

According to the process to this invention, it is possible to synthesize the crystalline complex perovskite type compounds at a low temperature of around 100°C, which is 500 to 700°C lower than the temperature required in the conventional methods, by adjusting the amount of water added according to the type of the solvent used and controlling the reaction temperature at a specified level or higher.

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
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X	PATENT ABSTRACTS OF JAPAN, vol. 9, no. 222 (C-302)[1945], 9th September 1985; JP - A - 60 086 026 (MISUBISHI KOGYO CEMENT K.K.) 15-05-1985 ----	1-3	C 01 G 53/00 C 01 F 11/00 C 01 B 13/32
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The present search report has been drawn up for all claims			
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<b>CATEGORY OF CITED DOCUMENTS</b>			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		I : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	

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